

Synthesis of Pu-Doped Ceramic

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ABSTRACT

Plutonium-doped zircon containing about 10 wt% Pu was synthesized in this cooperative project between Russia and the United States conducted at the V. G. Khlopin Radium Institute. The sol-gel method was used for starting precursor preparation to provide complete mixing of initial components and to avoid dust formation inside the glove-box. The sol-gel process also gives interim Pu stabilization in the form of amorphous zirconium hydrosilicate (AZHS), which is a result of gel solidification. AZHS is a solid and relatively durable material that can be easily converted into crystalline zircon by pressureless sintering, thus avoiding significant radioactive contamination of laboratory equipment. A methanol-aqueous solution of tetraethoxysilane $\text{Si}(\text{OC}_2\text{H}_5)_4$, Pu-nitrate, and zirconil oxynitrate was prepared in final stoichiometry of zircon $(\text{Zr,Pu})\text{SiO}_4$ 80 wt% + zirconia $(\text{Zr,Pu})\text{O}_2$ 20 wt%. Gelation occurred after 90 hours at room temperature. AZHS with excess of zirconia 20 wt% was obtained as an interim calcine product and then it was converted into zircon/zirconia ceramic by sintering at 1490 to 1500°C in air for different time periods. The samples obtained were studied by SRD and ESEM methods. It was found that both zircon yield and zircon cell parameters that are correlated with Pu incorporation depend on sintering time.

1. INTRODUCTION

The choice of zircon as the plutonium host-phase and justification of its durability are based on previous studies [1-10, 13]. Most earlier experiments on zircon synthesis were carried out using a Ce admixture as the Pu-simulant [10, 13]. However, there was information about successful synthesis of Pu-doped zircon containing 10 wt% ^{238}Pu [14]. Because the technological problems associated with providing a full stoichiometry of a starting precursor synthesis of 100% zircon-based ceramic are difficult, we decided to use a zircon/zirconia-based ceramic (80-90% zircon and the rest zirconia). This allowed us to apply a non-stoichiometric precursor with an excess of Zr [4, 8-10]. The

goal of this work was to study in detail the physico-chemical properties of Pu-doped zircon/zirconia ceramic, in particular the features of the zircon-Pu host-phase.

2. EXPERIMENTAL

Pu oxide (mostly ^{239}Pu) powder was dissolved in nitric acid while heating for 16 hours inside a specially designed glove-box (Fig. 1a). A methanol-aqueous solution of tetraethoxysilane $\text{Si}(\text{OC}_2\text{H}_5)_4$, Pu-nitrate and zirconil oxynitrate was prepared in final stoichiometry of zircon $(\text{Zr,Pu})\text{SiO}_4$ 80 wt% and 20 wt% zirconia $(\text{Zr,Pu})\text{O}_2$. Generally, the Pu content provided for the final ceramic was about 10 wt% (estimated for Pu metal). Gelation occurred after 90 hours at room temperature. The solidified gel of yellow-green color obtained was transparent (Fig. 1b), and no inclusions or sediments were found by optical microscopy. The solid gel was slowly heated in the air at 330°C for 1 hour to release most of the nitrogen oxide. Amorphous zirconium hydrosilicate (AZHS) with excess of zirconia about 20 wt% was obtained as interim calcine product. Then some of the pieces of AZHS, 1 to 1.5 cm in size, were heated in an alumina crucible up to 1500°C and sintered at this temperature in air for over 1 hour. Another portion of the AZHS pieces were ball milled in wet (water) media for 2 hours, and cold pressed into pellets 0.8 cm in diameter and 0.5 cm in height. Then these pellets were sintered in air at 1490–1500°C, some for 1.5 hours and others for 3 hours, 15 min. The samples obtained were studied by x-ray diffraction (XRD) and scanning electron microscopy (ESEM) methods.

3. RESULTS AND DISCUSSION

The features of the synthesized samples are summarized in Table 1. In comparison with the first two samples, the third does not contain a significant amount (more than 0.5 wt%) silica as cristobalite or amorphous forms; therefore, it can be considered to be the result of complete synthesis. A separate pure PuO_2 phase was not found in the matrices of

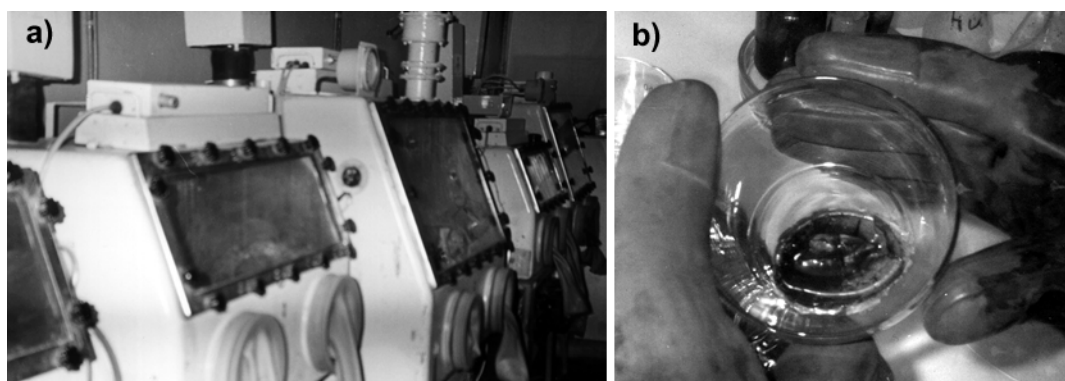


Figure 1. (a) The chain of glove-boxes used for Pu-ceramic fabrication and (b) the solidified Pu-containing gel for the synthesis of zircon/zirconia ceramic.

Table 1. Features of Pu-ceramic samples synthesized by sintering in air.

#	Starting precursor	Sintering conditions		Ceramic density (g/cm ³)	Yield in wt%			Zircon cell parameters (angstroms)
		Time (H:min)	Temp. (°C)		Zircon	Mono-clinic zirconia	Tetra-gonal zirconia	
1	Nonmilled AZHS	1	1490	3.1-3.2	10-20	40	20	a = 6.597±0.005 c = 5.972±0.006
2	Milled and cold pressed AZHS	1:30	1500	3.27	75	1	10	a = 6.609±0.004 c = 5.984±0.004
3	Milled and cold pressed AZHS	3:15	1490	3.72	80	1-3	15	a = 6.615±0.004 c = 5.990±0.004

all samples, despite the fact that Sample 2 contains about 10 wt% and Sample 3 contains about 1 to 3 wt% of a not clearly identified Pu-Zr-oxide phase, probably $(\text{Pu}_{0.5}\text{Zr}_{0.5})\text{O}_2$. It is important to note that Pu incorporation in zircon lattice (and as a result, increasing cell parameters) was correlated with time of sintering (Table 1). Probably this means that Pu distribution in zircon microcrystals is not homogeneous: central parts of the crystals have a lower Pu content than peripheral ones. The same situation was found earlier for the crystals of high-uranium zircon from Chernobyl lava [1, 2]. Monoclinic and tetragonal zirconia phases in all samples are also characterized by shifted peaks on x-ray diffraction spectra, which without doubt are caused by Pu incorporation into their lattices. ESEM examination has shown that generally zircon and zirconia phases in matrices of all samples form homogeneous mixtures with particle sizes less than 1 micron. However, some relatively large particles (20–30 microns in size) of Pu-containing zirconia can be also observed. Unreacted silica (Samples 1 and 2) forms separate inclusions 10 to 30 microns in size, and does not contain Pu admixture (detection limit, 0.1 wt%).

CONCLUSIONS

The results obtained allow us to make the following conclusions:

- Successful synthesis of 10 wt% ^{239}Pu -doped zircon/zirconia ceramic was carried out by sintering in air at 1490°C from the precursor fabricated by the sol-gel process.
- Sintering of AZHS at 1490°C for 3 hours 15 minutes provided almost a complete yield of Pu-doped zircon/zirconia host-phases, avoiding any remaining unreacted silica and the formation of a separate PuO_2 phase.
- Pu incorporation took place in the zircon lattice. As a result, increasing cell parameters are correlated with the time of sintering. As assumed, zircon microcrystals have a zonal Pu distribution in their matrices with less Pu content in the central parts and the highest Pu content in the peripheral parts.

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REFERENCES

1. Anderson, E.B., B. E. Burakov, and E. M. Pazukhin (1993) "High-Uranium Zircon from 'Chernobyl Lavas,' *Radiochimica Acta* **60**, 149-151.
2. Burakov, B.E. (1993) "A Study of High-Uranium Technogenous Zircon (Zr,U)SiO₄ from Chernobyl 'Lavas' in Connection with the Problem of Creating a Crystalline Matrix for High-Level Waste Disposal," *Proc. International Conference SAFE WASTE-93*, 13-18/06/1993, Avignon, France, vol. 2, 19-28.
3. Burakov, B.E, E. B. Anderson, E. M. Pazukhin, and E. E. Mikhcheva (1991) "A Method for Obtaining Crystalline Zircon Doped with Isomorphous Admixtures," Patent of Russia by the Application No. 5020357/26 of November 12 (in Russian).
4. Anderson, E.B, E. B. Burakov, and V. G. Vasiliev (1993) "A Creation of Crystalline Matrix for Actinide Waste in Khlopin Radium Institute," *Proc. of International Conference SAFE WASTE-93*, 13-18/06/1993, Avignon, France, vol. 2, 29-33.
5. Anderson, E.B, B. E. Burakov, B. Ya Galkin, et al. (1995) "UK-Russian Collaboration High Level Waste Immobilization Studies," *Proc. International Conference Global-95*, Versailles, France, 11-14/09/1995, vol. 1, 216-223.
6. Ewing, R.C, W. Lutze, and W. J. Weber (1995) "Zircon: A Host-Phase for the Disposal of Weapons Plutonium," *J Material Research* **10**, 243-246.
7. Ewing, R.C, W. J. Weber, and W. Lutze (1996) "Crystalline Ceramics: Waste Forms for the Disposal of Weapons Plutonium," Eds. E.R. Merz and C.E. Walter, *Disposal of Weapon Plutonium*, 65-83, Kluwer Academic Publishers, Dordrecht.
8. Burakov, B.E, E. B. Anderson, B. Ya Galkin, V. A. Starchenko, and V. G. Vasiliev (1996) "The Crystalline Host-Phases for Immobilization of Weapons Plutonium and Waste Actinides," Eds. E.R. Merz and C.E. Walter, *Disposal of Weapon Plutonium*, 85-89, Kluwer Academic Publishers, Dordrecht.
9. Burakov, B. E, E. B. Anderson, and S. I. Shabalev (1998) "A Search of the Most Optimal Forms of the Solidification of High-Level Waste Geologically Compatible with Hosting Granitoid Rocks," *Defense Nuclear Waste Disposal in Russia*, Eds. M.J. Stenhouse and V.I. Kirko, *Proc. NATO Advanced Research Workshop*, Krasnoyarsk, Russia, June 25, 1996, Kluwer Academic Publishers, 59-68.
10. Burakov, B.E, E. B. Anderson, S. I. Rovsha, S. V. Ushakov, R. C. Ewing, W. Lutze, and W. J. Weber (1996) "Synthesis of Zircon for Immobilization of Actinides," *Materials Research Society Symposium Proceedings: Scientific Basis for Nuclear Waste Management XIX*, vol. 412, 33-39.
11. Helean, K.B, B. E. Burakov, E. B. Anderson, E. E. Strykanova, S. V. Ushakov, and R. C. Ewing (1997) "Mineralogical and Microtextural Characterization of 'Gel-Zircon' from the Manibay Uranium Mine, Kazakhstan," *Materials Research Society Symposium Proceedings: Scientific Basis for Nuclear Waste Management XX*, vol. 465, 1219-1226.
12. Burakov, B.E, K. B. Helean, E. B. Anderson, and R. C. Ewing (1997) "Amorphous Zirconium Hydrosilicate (AZHS)—a Prospective Material for Plutonium Fixation," *Trans. International Conference Plutonium Futures—the Science*, Santa-Fe, New-Mexico, USA, August 25-27, 1997, p. 21.
13. Ushakov, S.V, B. E. Burakov, V. M. Garbuzov, E. B. Anderson, E. E. Strykanova, M. M. Yagovkina, K. B. Helean, Y. X. Guo, R. C. Ewing, and W. Lutze (1998) "Synthesis of Ce-Doped Zircon by a Sol-Gel Process," *Material Research Society Symposium Proceedings: Scientific Basis for Nuclear Waste Management XXI*, vol. 506, 281-288.
14. Exarhos, G.J. (1984) "Induced Swelling in Radiation Damaged ZrSiO₄," *Nuclear Instruments and Methods in Physics Research B1*, North-Holland, Amsterdam, Elsevier Science Publisher B.V., 538-541.